



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

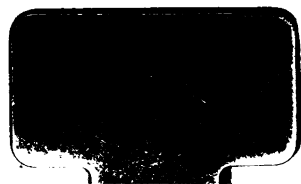
About Google Book Search

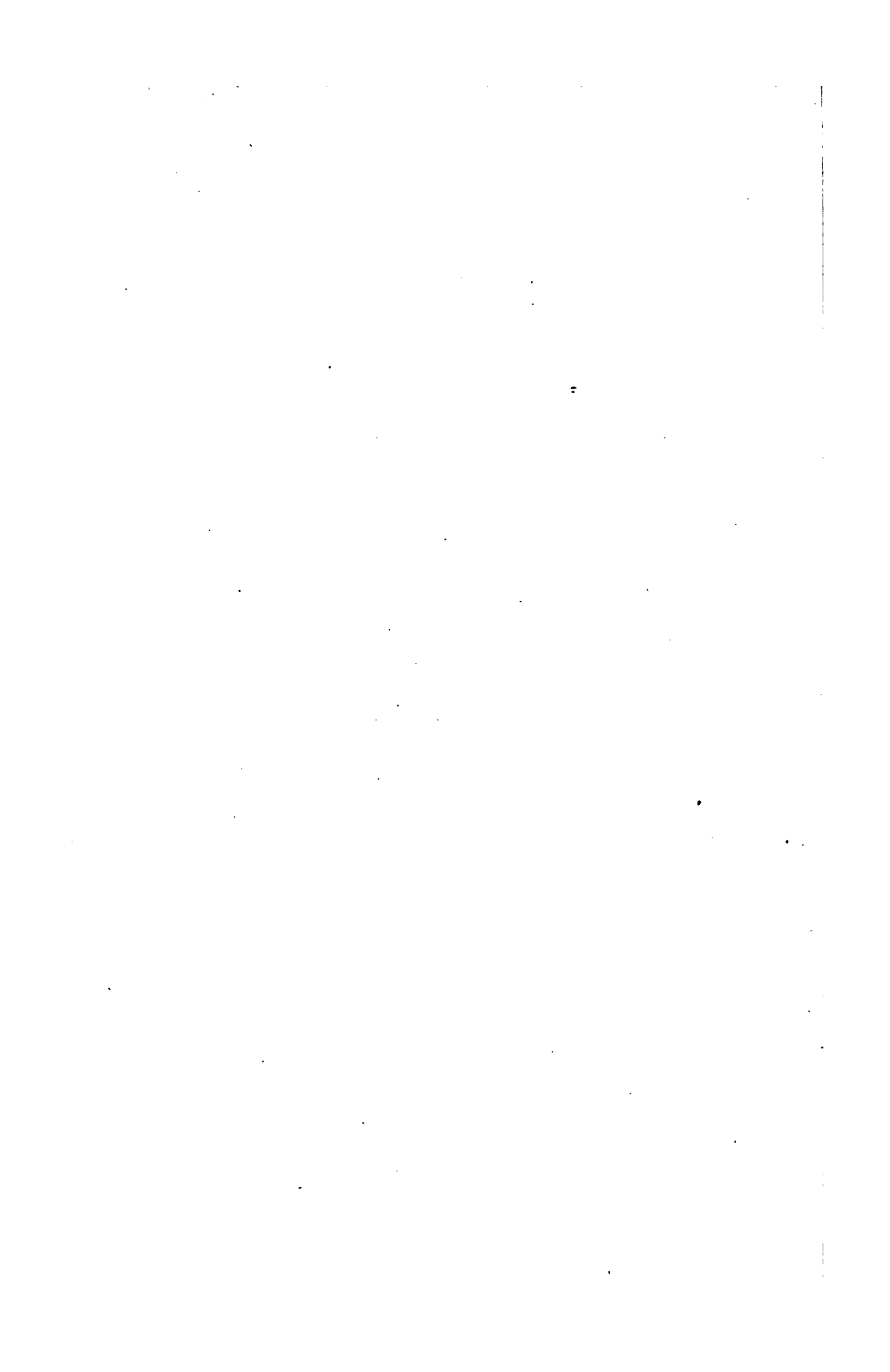
Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

ANILINE BLACK.

193. e.

43.





THE
CHEMICAL HISTORY AND PROGRESS
OF
ANILINE BLACK.

BY
JOHN LIGHTFOOT, CHEMIST.



PUBLISHED BY THE AUTHOR AT
LOWER HOUSE, BURNLEY, LANCASHIRE.

—
1871.

193. e. 43.

LONDON :
BENJAMIN TIPPER AND SON, PRINTERS, 10, CLOAK LANE,
CANNON STREET, E.C.

P R E F A C E.

THE object of the present pamphlet is to give to the Chemists and others connected with Dyeing and Calico Printing, the true History and Progress of Aniline Black during the past ten years, as well as some curious experiments made with the purpose of determining many vexed and debated points in connection therewith.

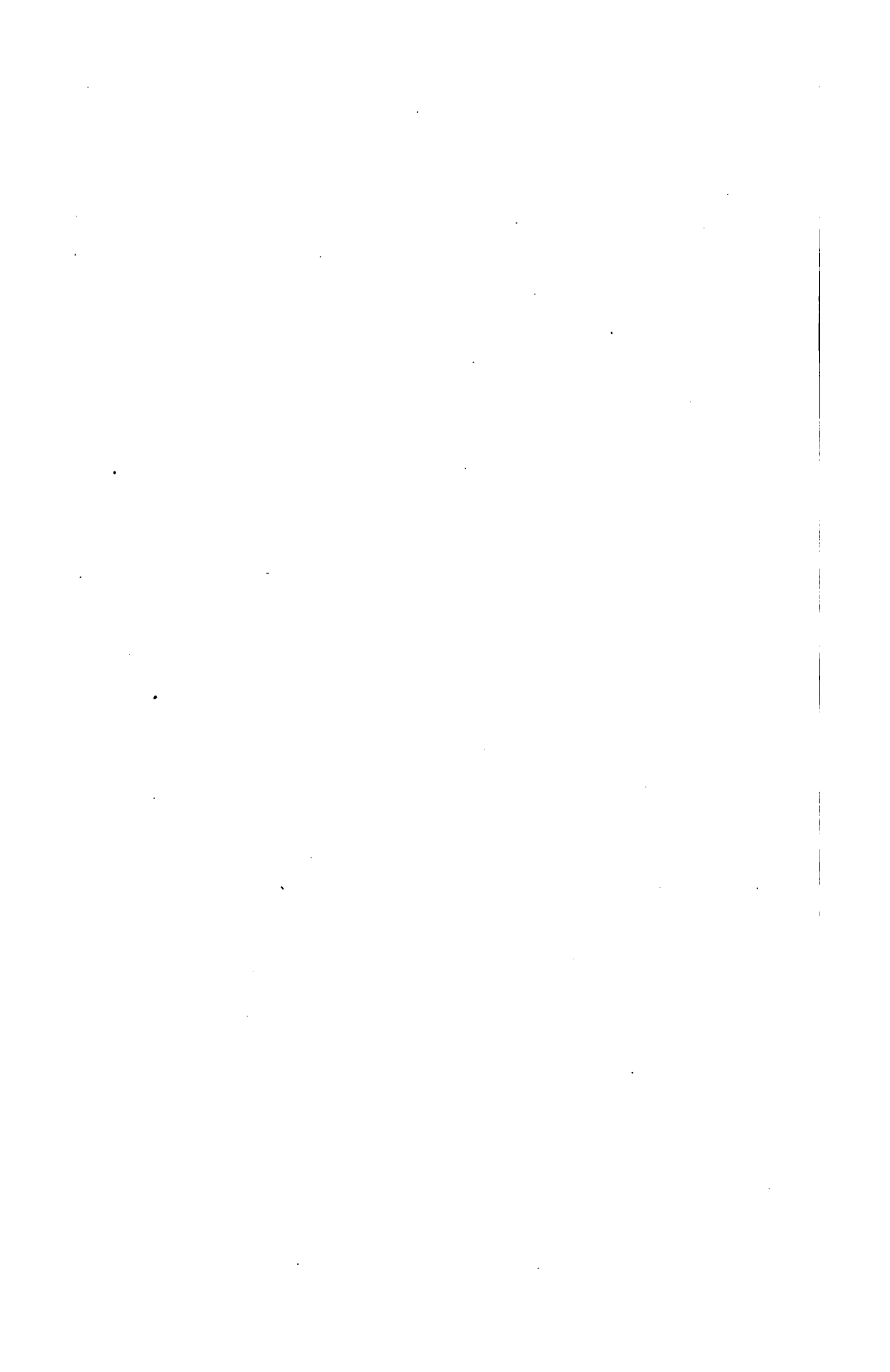
As the inventor and first producer of the Aniline Black upon calico, I have naturally wished to overcome any difficulties in using it, and to add from time to time to our information of its properties, and the mode of its formation.

Up to the present time, no very certain or well-defined theory has perfectly accounted for this product of Aniline; and if my experiments will not even now explain it, I may at least hope to add to the amount of knowledge we already possess upon this permanently fast black.

JOHN LIGHTFOOT.

LOWER HOUSE, BURNLEY,

May 1, 1871.



ANILINE BLACK.

IN the year 1859, I was working out some experiments upon aniline for Mr. Richard Dugdale Kay, of Accrington, which he had sent to me as oil of naptha; the market price of it was then from 15s. to 20s. per lb.

In November, of the same year, I found that by mixing an acid chloride of aniline (equal parts of pure hydrochloric acid and aniline) with starch paste, holding 4 ozs. of chlorate of potash per gallon, and printing the mixture with a wood block, that little or no colour was produced after twenty-four hours' ageing; but that when the same colour was printed in the machine with the copper roller, a green colour was produced in twelve hours.

My notice of this strange fact was the cause that led me to the discovery of the aniline black. I at once repeated this mixture, and added to it various proportions of nitromuriate of copper, 88° T., and I then found that the intensity of the black was dependent upon the proportions of copper and aniline salt employed, as well as the duration of the ageing.

The colour, when first printed, was a pale olive, which gradually developed into the fibre to an intense myrtle green, in about twenty-four hours. When washed in water *only*, without alkali or soap, it became an intense black.

Subsequent experiments of M. Rosentheil and others have proved that the mixture of chloride of aniline, starch paste, and chlorate of potash, made in an earthen vessel, does not give much colour if printed with a wood block.

The colour I made was mixed in a copper vessel, and this, with the copper rollers, gave me the dark green that I printed in November, 1859; but the true black itself was not produced until the salt of copper was added to the mixture.

The high price of aniline at this time prevented me thinking much of the black, except as a chemical curiosity; but I had sufficiently developed the colour to print a few pieces of calico in July, 1860, at the Broad Oak Print Works, Accrington, from the following mixture:—

Starch paste (1½ lbs. per gallon)	1 gallon.
Chlorate of potash	4 ozs.
{ Aniline (oil of naptha)	8 „
{ Hydrochloric acid, 32° T.	8 „
Sal ammoniac	4 „
Nitrate of copper, 88° T.	2 „

This colour was printed with madder pink ground, aged two nights; then the black and pink passed through "Higgins'" alkaline arseniate of soda, mixed with water at 180° F., washed, dunged, dyed in madder, and soaped.

Except a few pieces of single blacks, nothing more was done till the end of the year 1862, when an offer was made for the process by Messrs. J. J. Müller and Co., of Basle, Switzerland, which resulted in it being patented in January, 1863, and sold to them.

My own personal account of the share I had in the discovery may be concluded with the following correspondence from the "Chemical News":—

" 'Chemical News,' December 6, 1862.

"BLACK DYE FROM ANILINE.

" *To the Editor of the Chemical News.*

"SIR,—There have been many colours produced from 'aniline' and its analogues, namely, violets, pinks, blues, etc., but I have not seen or heard of a good black that has been produced from aniline, capable of being printed or dyed along with the above-named colours, excepting one that was discovered by me about two years ago; and I now take the opportunity of enclosing you swatches of my new black from aniline (dyed and printed) for your inspection and trial.

"This black has peculiar properties, being perfectly fast, and not affected either by light or being boiled for several hours in a strong

solution of soap. Strong sulphuric acid destroys the cotton, but leaves a black or purple pigment behind. Strong caustic soda does not injure the colour, even if boiled, and the strongest solution of hypochlorite of lime does not affect it in the least; in fact, all the chemical agents I have tried will not discharge it. It is a valuable black for Turkey-red styles; and when printed along with madder colours it fixes 'perfectly fast,' and does not take the dye from the madder-bath; hence its value as a substitute for chemical black. It is also valuable as an 'indelible ink,' and for marking grey goods, as a substitute for 'tar.'

"If you will kindly insert this in your next journal, perhaps some of your numerous correspondents will suggest some other use for this 'indestructible black.' I simply bring this before your notice, lest it should be claimed by some other colourist or chemist at some future time.

"I am, etc., "JOHN LIGHTFOOT.

"Broad Oak Laboratory, Accrington, Lancashire.

"[The colour is not a pure black, and does not look so well in the solid as in the printed specimens, which show extremely well. Chlorine will almost discharge the colour.—ED. C. N.]"

NOTE.—C. Kœchlin has since noted the fact that, though apparently discharged by chlorine, the black returns in all its intensity in a few days.

" 'Chemical News,' December 20, 1862.

"BLACK DYE FROM ANILINE.

"*To the Editor of the Chemical News.*

"SIR,—Having seen a notice of a new black from aniline in a recent number of the 'Chemical News,' I would state, that some time ago I obtained on cotton fabric a black from aniline, capable of resisting acids, alkalies, and other re-agents to a very remarkable extent, and which was very difficult to discharge.

"I am, etc., "W. CORT WRIGHT.

"Laboratory, Bank Bridge, near Manchester."

" 'Chemical News,' January 3, 1863.

"BLACK DYE FROM ANILINE.

"*To the Editor of the Chemical News.*

"SIR,—In reply to a notice in the 'Chemical News' of Decem-

ber 20, 1862, and signed by Mr. W. Cort Wright, I beg to say that I have seen a black from aniline, dyed and printed in July, 1860, which was discovered by Mr. John Lightfoot, jun., Broad Oak Print Works, Accrington, a swatch of which I beg to enclose.

"I am, etc., "J. C. DERBYSHIRE.

"Church, near Accrington."

[M. Emile Gatty preserved a specimen of this black, printed and given to him in 1860, and returned it to me in 1863.]

The following patents, more or less connected with the history of the aniline black, are given in their chronological order. Only so much of their subject matter, in the less important ones, is indicated as is necessary to understand the remarks attached to them :—

Almost the earliest, if not *the* earliest, mention of aniline black, will be found in the patent of

Dale and Caro, 1860, 26th May, No. 1,307,

for "obtaining colouring matters of purple and red shades from pure or commercial aniline."

Salts of aniline, mixed with solutions of perchloride of copper, were heated, which gave a "black or dark purple precipitate." The purple colouring matter is extracted, first with hot water and then with alcohol, "until the whole of the purple colouring matter has been dissolved out."

The patent does not expressly mention the black residue left from the washings, but the black residue has for a long time been sold by Messrs. Roberts, Dale and Co., of Manchester, under the name of "Aniline Black Pigment." It is, perhaps, the best black known for "topical" printing with albumen colours, as it does not tarnish the "ginguets green," or "ultramarine blue," *like the logwood black*.

Calvert, Lowe and Clift, 11th June, 1860, No. 1,426,

Patent for "the production of a green insoluble colouring matter from aniline, by oxidation directly in contact with the yarn tissue or fabric," termed "emeraldine," and the "conver-

sion of the green colouring matter, thus obtained, into a blue colouring matter by the action of alkalies," termed "azurine."

The formula given is as follows :—

"Solution of an acid salt of aniline (containing 1 lb. of aniline).

Tartrate, or chloride of aniline 3 lbs.

Starch, or flour paste 60 "

Chlorate of potash 1 " "

"The goods must be allowed to age for twelve hours, by which time the colour will be completely developed."

"To convert the green colour, obtained as above described, into azurine of a blue or purple shade, the goods must be boiled in a weak alkaline, or soap solution, and dried;" "or the goods may be passed into a weak solution of chromate or bichromate of potash, previously to being washed off."

In the "Journal of the Society of Arts," February 7th, 1862, Dr. F. Crace Calvert, in a lecture before the Society, notices this process as follows :—

"GREEN COLOURS FROM ANILINE.—Although it has been known to chemists that aniline would yield a green colour under certain oxidising agents, up to the present time all efforts to dye silk or wool commercially with it have failed; but to avoid having to refer to this green colour again, I may mention that Messrs. Cliff, Charles Lowe, and myself patented, on the 11th June, 1860, a most easy and practical method of producing it, under the name of *emeraldine*, on cotton fabrics, specimens of which I have the honour to show you. The process consists in printing an acid chloride of aniline on a cotton fabric prepared with chlorate of potash, and in a few hours a beautiful bright green gradually appears, which only requires to be washed. If the green fabric is passed through a solution of bichromate of potash, this colour is transformed into a dark indigo blue, called by us *azurine*."

The following extract is taken from the "Chimie Organique de Girardin," 1861, but probably refers to the account of Willm's experiments, given to the Société Industrielle de Mulhouse, February, 1860 :—

"If you print upon calico a mixture of muriate of aniline, acetic acid and chlorate of potash, and hang it up, it becomes green in a

few hours. After that pass it through an alkaline bath, the colour from green becomes blue ; and if you have a strong proportion of aniline salt, it becomes quite black."

But little practical application came of this patent, on account of its liability to turn green under the influence of the slightest acidity. It was not quite fast to soap, and never, under the conditions stated, became other than an intense blue. Black has never been made with it, when those conditions have been carefully fulfilled.

Although out of the regular chronological order, it will be best, perhaps, to mention the following extracts from Dr. F. Crace Calvert's "Dyeing and Calico Printing," in reference to this particular patent. They appear in a second enlarged edition of the lecture above quoted, and they will be found in a copy which was deposited in the British Museum the 10th of April, 1863. The book has no date, has not been found in the Stationers' Hall register, and bears internal evidence that it appeared subsequently to the date of application of the Lightfoot Patent :—

"The production of this colour directly on the fabric, is most important, and it will probably lead to the similar production of the other coal-tar colours, without previous treatment, directly on the cloth. By this means, not only the great loss of aniline in the original production of the colour, will be avoided, but a considerable economy of mordants will be effected.

"These gentlemen also induced Messrs. Wood and Wright, at the end of 1860, to produce, by their process, dark green or blue which they considered sufficiently good to be introduced into the market, and Messrs. Wood and Wright have further effected an improvement in these dark shades, which may be called black, by adding to the chlorate of potash, persalts of iron or other oxydising agents ; also by oxydising the colour thus produced on the fabric (which is the chief novelty of this process), either by a weak solution of bi-chromate of potash, or bleaching-powder. Nitrate of copper may be mixed with the hydrochlorate of aniline, without the addition of chlorate of potash, and the mixture printed on the fabric, when gradually a dark green or black is produced. This mode of printing directly on the fabric, gives green or blue, so dark as to be almost identical with black.

"Dark blues, imitating indigo, have also been produced, on a

commercial scale, by this process, and its success was such that if the colour had not been affected by acids, it would have superseded most of the indigo styles."

In reference to these divers products from aniline and chlorate of potash, Kopp ("Moniteur Scientifique," 1861) says that they are all one substance, of which the shade depends upon the acidity or neutrality of the mixture; but *he considers them fast* to light and to soap.

A.D. 1863. 17th January. No. 151.

PRINTING AND DYEING TEXTILE FABRICS AND YARNS.

LETTERS PATENT to John Lightfoot, of Accrington, in the County of Lancaster, Chemist, for the Invention of "Improvements in Printing and Dyeing Textile Fabrics and Yarns."

Scaled the 24th March, 1863, and dated the 17th January, 1863.

PROVISIONAL SPECIFICATION left by the said John Lightfoot at the Office of the Commissioners of Patents, with his Petition, on the 17th January, 1863.

I, John Lightfoot, of Accrington, in the County of Lancaster, Chemist, do hereby declare the nature of the said Invention for "Improvements in Printing and Dyeing Textile Fabrics and Yarns," to be as follows:—

These improvements consist in the production of a black colour on textile fabrics or yarns, by printing or staining them with a salt of aniline or any of its analogous mixed with certain oxidising agents hereafter described.

I take 1 gallon of water and dissolve in it 4 oz. of chlorate of potash; to this I add aniline, or any of its analogues, by preference aniline, in the proportion of 8 oz. per gallon, and an equal weight of hydrochloric acid. After stirring well I add 1 pint of acetic acid per gallon, and 8 oz. measure of perchloride of copper at 88° Twaddell, 4 oz. of salammoniac, or an equivalent quantity of other alkaline chloride. I steep the fabric or yarn in this solution, wring out and dry, age two nights, and pass through a weak solution of alkali or soap, or, by preference, diluted hypochlorite of lime. An intense black is thus produced.

For printing on fabrics or yarns I take 1 gallon of starch paste, or other suitable thickening, and dissolve in it 4 oz. chlorate of potash, 8 oz. aniline, 8 oz. hydrochloric acid, and 4 oz. measure of

perchloride of copper at 88° Twaddell, and 2 oz. salammoniac, or an equivalent quantity of other alkaline chloride. After printing this colour I age three nights, and raise in weak alkali or soap, or hypochlorite of lime, as before.

I do not confine myself to perchloride of copper, as other salts of copper will do if mixed with alkaline chlorides; and in some cases I use instead of copper salts of chlorides of antimony, or chlorides of iron.

SPECIFICATION in pursuance of the conditions of the Letters Patent, filed by the said John Lightfoot in the Great Seal Patent Office on the 16th July, 1863.

TO ALL TO WHOM THESE PRESENTS SHALL COME, I, John Lightfoot, of Accrington, in the County of Lancaster, Chemist, send greeting.

WHEREAS Her most Excellent Majesty Queen Victoria, by Her Letters Patent, bearing date the Seventeenth day of January, in the year of our Lord One thousand eight hundred and sixty-three, in the twenty-sixth year of Her reign, did, for Herself, Her heirs and successors, give and grant unto me, the said John Lightfoot, Her special license that I, the said John Lightfoot, my executors, administrators, and assigns, or such others as I, the said John Lightfoot, my executors, administrators, and assigns, should at any time agree with, and no others, from time to time and at all times thereafter during the term therein expressed, should and lawfully might make, use, exercise, and vend, within the United Kingdom of Great Britain and Ireland, the Channel Islands, and Isle of Man, an Invention for "Improvements in Printing and Dyeing Textile Fabrics and Yarns," upon the condition (amongst others) that I, the said John Lightfoot, my executors or administrators, by an instrument in writing under my, or their, or one of their hands and seals, should particularly describe and ascertain the nature of the said Invention, and in what manner the same was to be performed, and cause the same to be filed in the Great Seal Patent Office within six calendar months next, and immediately after the date of the said Letters Patent.

NOW KNOW YE, that I, the said John Lightfoot, do hereby declare the nature of my said Invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement, that is to say:—

These improvements consist in the production of a black dye on textile fabrics or yarns, by printing or staining them with a salt or salts of aniline, or any analogous, homologous, or isomeric com-

pounds, mixed with certain metallic salts, or their oxides, as a mordant, as hereinafter described.

I take 1 gallon of water and dissolve in it 4 oz. chlorate or potash; to this I add aniline, or any analogous, homologous, or isomeric matters, using, by preference, aniline in the proportion of 8 oz., previously combining it with 8 oz. of hydrochloric acid at 32° Twaddell. After stirring well, I add 1 pint of acetic acid and 8 oz. measure of perchloride of copper at 88° Twaddell; then I add 4 oz. salammoniac, or an equivalent quantity of other suitable alkaline chloride. I steep the fabric or yarn in this solution, wring out and dry, then I expose the goods in a room, at from 60° to 70° Fahrenheit, for two or three days; the goods are now passed through water alone, or a solution containing alkaline or metallic salts (which develop the black much sooner and better). The alkalis and alkaline earths may be used for raising the black, such as caustic soda, caustic potash, caustic ammonia, caustic lime in solution in water; or the goods may be passed, after "printing" and "dyeing," through a box containing rollers supplied with "ammoniacal gas" (which I prefer, when the black is printed along with "steam colours" prior to steaming the goods). When the black is printed along with "madder," or "garancine" colours, they are aged or exposed in a room, at from 60° to 70° Fahrenheit, for three days, and dunged, dyed, washed, and passed through a solution of soap or dilute hypochlorite of lime, whereby an intense black is produced.

For printing on fabrics or yarns, I take 1 gallon of starch paste (containing 1 lb. starch per gallon), or other suitable thickening ingredient, and dissolve in it 4 oz. chlorate of potash and 8 oz. aniline, previously combined with 8 oz. hydrochloric acid; I then add 4 oz. measure of perchloride of copper, at 88° Twaddell, and 2 oz. salammoniac, or an equivalent quantity of other suitable alkaline chloride. After printing this colour I age for three nights, and raise in water alone, or weak alkali, or soap, or hypochlorite of lime, as before. Although in the proportions given chloride of copper only has been named other metallic salts may be substituted, as antimony and iron; and when such other salts are used, they are employed in proportions equivalent to the proportion of copper named. In some cases I pad the cloth in a solution of any of the metallic salts named, either separately or mixed together, dry, and print or pad on a thickened salt of aniline in combination with chlorate of potash, age three to four nights, and finish as previously

stated; or I pad the cloth in a solution of any of the metallic salts named, as before. I then precipitate the oxide of the metal or metals used into the cloth by passing through a solution of alkali suitable to the metal used, wash, dry, and print or pad on a thickened acid salt of aniline in combination with chlorate of potash, age three or four nights, and finish as before.

I have named the production of a black by the use of aniline salts with certain metallic salts, or the analogues of aniline. By the analogues of aniline I mean naphthylamine or toluidine, and when certain shades of black are required, I use a mixture of aniline with these analogous bodies; but in all cases a certain quantity of a salt of aniline must be used for the production of a good black. And although I have described the use of the metallic salts of copper as used with aniline, I find that these salts may be replaced with some advantages by the use of the salt known as red prussiate of potash; and when this salt is used it is used in substitution of other metallic salts, and I use it in the proportion of 4 to 6 oz. red prussiate of potash to 1 lb. of a salt of aniline, or mixtures of aniline and its analogues, contained in 1 gallon of water. When red prussiate of potash is used, I also add to each gallon of colour 2 oz. oxalic acid, or other suitable acid, by preference oxalic acid. The material to be dyed or printed must be first aged, and afterwards steamed thirty to fifty minutes in the ordinary manner of steaming.

I do not confine myself to the precise details herein mentioned, nor to the exact quantities herein stated, as they may be slightly modified without departing from the spirit of my Invention; but what I claim as my Invention is, the use of metallic salts or their oxides, either alone or combined with chlorate of potash, and then mixed with a salt or salts of aniline, or mixtures with any analogous, homologous, or isomeric compounds, either singly or mixed together, as well as the process, or series of processes, as previously described, for the production of a black dye or satin.

In witness whereof, I, the said John Lightfoot, have hereunto set my hand and seal, this Fifteenth day of July, in the year of our Lord One thousand eight hundred and sixty-three.

JOHN LIGHTFOOT. (L.S.)

Dr. Reiman, "Aniline and its Derivatives," edition by Mr. Crookes, says that—

"No real black can be found among the aniline dyes. In all

cases, what is called black is really dark green or brown. Real black cannot be obtained in dyeing, and is only represented by amorphous carbon ; it cannot be called a colour, but is rather the absence of every colour. Colours produce their impression on our eye by absorbing certain rays of the spectrum, and reflecting others which thus enter our eye.

"We call black only those substances which absorb all the rays and reflect nothing ; from such a substance no ray can be reflected to the eye, and therefore from it we receive no optical impression.

"A substance really black is thus only seen in contrast with other coloured substances. Such a black, as stated above, is never found in dyeing : the black dyes are only dark blue, green, or brown ; and so, in this manner, may be explained why, although a real black can have no shades, there exists the well-known difference between blue black, greenish black, and brown black. If we succeed in obtaining an aniline colour so dark that it gives to the eye the ordinary impression of black, then we may consider that we have succeeded in producing aniline black."

Accepting this definition of black—the black by the chloride of copper is a true black—the eye cannot discover in good specimens a trace of any shade of colour, either blue, green, or brown, and it stands out in remarkable contrast to the dark blue shades, or *pseudo* blacks, of the previous processes. It is, in fact, the beautiful black pigment of Dale and Caro, originating, and indelibly fixed, in the fibre of the cloth.

In the first year of its publication it rapidly came into use, especially in Switzerland, where, in the year 1863, by hand printing more than 50,000 pieces were printed.

The roller printing was not so successful, from the acid chloride attacking both the steel doctor and the copper roller. The substitution of the chloride by the sulphate of copper, and the use of a neutral chloride of aniline, in some measure remedied the defects, but never quite overcame the attack upon the steel doctor. In spite of these drawbacks, it was nevertheless largely used, and is still employed where hand printing and dead roller work is employed.

The remarks upon this patent are so intermingled with the one of Charles Lauth, that it will be better to defer them, and embody them together, following Charles Lauth.

Frederick Albert Gatty, 1863, 25th February, No. 517.
This patent says—

“The cotton, or other fabrics, are impregnated with a mixture of acetate of alumina, and chromate of potash, or any other soluble chromate; and when dry they are printed with a thickened solution of a salt of aniline, or other similar tar product which forms the black colour.”

Very little application has been made of this patent. Any process requiring previous preparation is scarcely admissible commercially.

Honoré Cordillot, 1863, 4th December, No. .

Application of ferridcyanide of ammonium.

The colour was dear, decomposed rapidly, required a high temperature for the ageing, and attacked the cloth; inconveniences which caused its speedy abandonment.

A.D. 1864, 7th June, No. 1409.

“ DYEING AND PRINTING.

“LETTERS PATENT to Edward Joseph Hughes, of the city of Manchester, in the county of Lancaster, patent agent, for the invention of ‘Improvements in Dyeing and Printing.’ A communication from abroad by Charles Lauth, of Paris, in the Empire of France.

“Sealed the 2nd December, 1864, and dated the 7th June, 1864.

“PROVISIONAL SPECIFICATION left by the said Edward Joseph Hughes, at the office of the Commissioners of Patents, with his petition, on the 7th June, 1864.

“I, Edward Joseph Hughes, of the city of Manchester, in the county of Lancaster, patent agent, do hereby declare the nature of the said invention for ‘Improvements in Dyeing and Printing,’ being a communication to me from abroad by Charles Lauth, of Paris, in the Empire of France, to be as follows:—

“This invention consists in the production of a black colour on cotton or linen cloth or yarns, and I produce such black colour by the admixture of a salt of aniline with chlorate of potash and sulphuret or sulphide of copper, or sulphuret or sulphide of iron, or

mixtures of the same, the proportions being about 16 ozs. salt of aniline, 4 ozs. sulphide of copper, and 4 ozs. chlorate of potash to one gallon of water. I am aware that a black has before been produced by the admixture of a salt of aniline with soluble salts of copper, but the use of such soluble salts of copper has been found attended with such difficulties as to render it almost useless. These difficulties are entirely overcome by the use of sulphide of copper or iron with the salt of aniline and chlorate of potash in about the proportions already described when the black is required to be printed. When I dye black by this process I first precipitate in the cloth or yarn the sulphide of copper or iron, and subsequently pass through a solution of a salt of aniline and chlorate of potash. The cloth or yarn is afterwards dyed and washed when the black colour is produced.

“SPECIFICATION in pursuance of the conditions of the letters patent filed by the said Edward Joseph Hughes in the Great Seal Patent Office, on the 6th December, 1864.

“To all to whom these presents shall come, I, Edward Joseph Hughes, of the city of Manchester, in the county of Lancaster, patent agent, send greeting.

“Whereas Her Most Excellent Majesty Queen Victoria, by her letters patent, bearing date the seventh day of June, in the year of our Lord one thousand eight hundred and sixty-four, in the twenty-seventh year of her reign, did, for herself, her heirs and successors, give and grant unto me, the said Edward Joseph Hughes, her special license that I, the said Edward Joseph Hughes, my executors, administrators, and assigns, or such others as I, the said Edward Joseph Hughes, my executors, administrators, and assigns, should at any time agree with, and no others, from time to time and at all times thereafter during the term therein expressed, should and lawfully might make, use, exercise and vend within the United Kingdom of Great Britain and Ireland, the Channel Islands, and Isle of Man, an invention for ‘Improvements in Dyeing and Printing,’ being a communication to me from abroad by Charles Lauth, of Paris, in the Empire of France, upon the condition (amongst others) that I, the said Edward Joseph Hughes, my executors or administrators, by an instrument in writing under my or their or one of their hands and seals, should particularly describe and ascertain the nature of the said invention, and in what manner the same was to be performed, and cause the same to be filed in the

Great Seal Patent Office within six calendar months next and immediately after the date of the said Letters Patent.

"Now know ye that I, the said Edward Joseph Hughes, do hereby declare the nature of the said invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement (that is to say):—

"This invention consists in the production of a black colour on cotton or linen cloth or yarns, and I produce such black colour by the admixture of a salt of aniline with chlorate of potash and sulphuret or sulphide of copper, or sulphuret or sulphide of iron, or mixtures of the same, the proportions to be about 16 ozs. salt of aniline, 4 ozs. sulphide of copper, and 4 ozs. chromate of potash, to one gallon of water. I am aware that a black has before been produced by the admixture of a salt of aniline with soluble salts of copper, but the use of such soluble salts of copper has been found to be attended with such difficulties as to render it almost useless. These difficulties are entirely overcome by the use of sulphide of copper or iron with the salt of aniline and chlorate of potash, in about the proportions already described, when the black is required to be printed. When I dye black by this process, I first precipitate in the cloth or yarn the sulphide of copper or iron, and subsequently pass through a solution of a salt of aniline and chlorate of potash. The cloth or yarn is afterwards aged and washed, when the black colour is produced.

In witness whereof, I, the said Edward Joseph Hughes, have hereunto set my hand and seal, this Fifth day of December, in the year of our Lord one thousand eight hundred and sixty-four.

E. J. HUGHES. (L.S.)

ON ANILINE BLACK, BY M. LAUTH.

Bulletin de la Société Chimique, Dec., 1864.

"Aniline Black is a new coloured product, derived from aniline, and completes, in some sort, the series of brilliant colours which this base gives.

"This product differs in all respects from the other colouring matters derived from aniline; in its manner of production, its fixing upon the tissues, its permanence against physical and chemical agents, these are all points in which it differs essentially from aniline red, blue, or violet.

"In January, 1863, Mr. John Lightfoot, of Accrington, patented in France a process by which he obtained upon cotton, in printing and dyeing, a new black, called Aniline Black. This process consists in printing or dyeing with a mixture of—

Chlorate of potash	.	.	.	25 grammes.
Aniline	.	.	.	50 "
Hydrochloric acid	.	.	.	50 "
Perchloride of copper (of 144°)	.	.	.	50 "
Sal ammoniac	.	.	.	25 "
Acetic acid	.	.	.	12 "
Starch paste	.	.	.	1 litre.

The tissue, printed and dried, is exposed to the air (in oxidising chambers) about two days. After this time, it is washed in water, slightly alkaline, and the black, which is developed in the oxidising chamber, is found fixed.

"The point altogether new in this application is this, the colour does not exist when the mixture above is printed; it is only developed upon the tissue, and when by the concentration and a certain rise of temperature, the substances put in presence of each other are capable of re-acting.

"The acid of the salt of aniline determines the decomposition of the chlorate of potash; at the same time the chloride of copper re-acts upon the aniline, and these two oxidising actions combined, give rise to the formation of the new colour, which is completely insoluble, and then rests intimately fixed in the tissue.

"This process of Lightfoot presents serious inconveniences, and which caused its use to be abandoned.*

"My process consists in printing with the aniline salt and the chlorate of potash, an insoluble oxidising salt, but becoming soluble upon the tissue—for example, the sulphide of copper. This sulphide is changed by the oxidising action of the chloric acid or the chlorine (which is set free by the re-action of the hydrochlorate of aniline, upon the chlorate of potash) into sulphate of copper, and from thence the conditions are the same as the Lightfoot process.

"The Aniline Black has an aspect altogether special—a very rich velvet black.

* This inconvenience applies only to the roller; impressions by hand are not liable to any defect or difficulty. In 1863, 50,000 pieces were printed by hand in Switzerland and Germany, literally following the first formula we have given in Lightfoot's Patent.

"It is completely insoluble in water, boiling soap, alkalies, and acids.

"These latter change it to green, but the alkalies bring back the original colour.

"The Aniline Black is worked by Messrs. J. J. Müller et Cie, of Basle, who have had the merit of divining its importance from its first appearance, and to continue its working, in spite of the great sacrifices and difficulties they have met with.

"The colour costs about 1 franc the litre ; compared with madder black, and garancine it saves the manufacturer about 4 francs the piece of 100 metres."

MONITEUR SCIENTIFIQUE, MAY, 1867.

Letter from Camille Kœchlin (to Dr. Quesneville).

"The citing my name, on the subject of Aniline Black, in your number of the 15th April, p. 313 is likely to lead to the supposition that I had something to do with the invention of that colour, and obliges me to disclaim against appearances of merit, so worthy of envy ; but which can never be disputed with Mr. Lightfoot.

"The chemist of Accrington alone, had the happy idea of Aniline Black. His process alone has survived all others. If the process has been modified, ameliorated, the elementary principles, determining the reaction, have nevertheless remained the same: copper, sal ammoniac, aniline salt, chlorate. Outside of this formula is only seen receipts more or less absurd, imagined by an unworthy plagiarism of a process offered to industry, with a moderation without example.

"The improvements introduced in the original receipt of Lightfoot, consisted in turning two inconveniences. The one compromised the tissue ; the other, compromising the engraved rollers, and metals, serving for the impression. The first, depended on the kind of salt of aniline, whether printing with chloride or nitrate, it was as to a textile fabric like covering it with nitric or hydrochloric acid. The second defect arose from the copper in a soluble state in contact with an aniline salt (chloride) and with sal ammoniac. The fate of the black remained in suspense before this last inconvenience, when a distinguished chemist came to draw us from our embarrassment, proposing for our oxidising compositions, an insoluble copper salt, absolutely innocuous to the metals, at the moment of the impression, and susceptible of becoming soluble, as soon as this has

been done. With the idea of the mineral of Charles Lauth, the invention of Lightfoot received its chemical completeness. It only remained to be put in practice ; a difficulty quite secondary, and to which alone your mention of our house could apply.

"When only one word is said about Aniline Black, on that colour, which the manufacturers will never pay for at its value, according to its worth, one should always precede it with gratitude for that man who, from Accrington where it was buried, knew how to propagate it, imposing on himself great sacrifices for its improvement. If, in the same manner, for citizens who deserve well of their country, one could say, J. J. Müller deserves well of the manufacturer, it would be the only reward of his enterprise up to this solemn moment, when the jury may consecrate, in a more worthy manner, the attestation of the manufacturers to the realiser of a colour, the most mentorious, which figures in the Exhibition.

"C. KÆCHLIN."

EXTRACTS FROM "ANILINE AND ITS DERIVATIVES," BY M. REIMANN, P.D., L.A.M., AND APPENDIX REPORT ON FRENCH EXHIBITION BY DR. A. W. HOFFMANN, F.R.S., M.M.G., DE LAIRE AND CHARLES GIRARD, EDITED BY WILLIAM CROOKES, F.R.S., 1868.

DR. REIMANN.

"In January 1863 a French Patent was granted him (J. Lightfoot) for printing calico with Aniline Black. This he sold to the firm of J. J. Müller and Co., of Basle, of whom we have before spoken. Mr. Lightfoot employs as agents, chlorate of potash, bichloride of Copper (Cu Cl_2), which, by giving up chlorine, is transformed into subchloride of copper ($\text{Cu}_2 \text{Cl}_2$),* hydrochlorate of aniline, acetic acid, to liberate chloric acid, and starch paste to thicken the mass. The paste thus made is used for printing, and then the tissue is hung up in oxidizing chambers and washed with weak alkali. The colour is developed in the oxidizing chambers by the mutual reaction of the chlorate of potash and chloride of copper.

"According to Mr. Kappelin, Lightfoot's paste consists of:—

6 litres of Water.

850 grammes of White Starch.

180 " of Chlorate of Potash.

450 " of Hydrochlorate of Aniline.

150 " of Sulphate of Copper.

* The original gives (Cu Cl_2), which is probably a misprint.

"In this specification the sulphate is employed instead of the chloride of copper.

"In 1864, Mr. Lauth took out a patent for a method of printing Aniline Black on calico, and by this process cotton is still printed with Aniline Black. Mr. Lauth's paste is the same as that of Mr. Lightfoot, but he adds the copper salt in the form of insoluble sulphide of copper, whereby its action on steel is prevented. After being printed, this compound being exposed to the influence of the atmosphere, or of the chlorate of potash in the paste, is transformed into a soluble salt, sulphate of copper, and now acts as the oxidising agent. The process is not expensive, and scarcely weakens the tissues at all.

"This patent black has also been bought by the firm of J. J. Müller and Co., of Basle."

Dr. HOFFMANN

Speaking of the Exhibition of 1862, he says—

"At that time Aniline Black only existed in theory, now (1867) it is one of the most valuable of this class of colours.

"The process patented by Mr. Lightfoot has this peculiarity, that the black colour does not exist at the moment the tissue is printed on, but is gradually developed on the fibre as the result of reactions which are set up between the bodies constituting the mixture, in contact with atmospheric oxygen at a certain temperature.

"It was not until January, 1865, that Mr. Lauth succeeded in remedying the principal inconveniences which attended the production of Aniline Black, produced by Mr. Lightfoot's process, by simply substituting sulphide for bichloride of copper. This sulphide is changed into sulphate by the oxidising action of the chloric acid, the chlorine, or one of the chloro-derivatives produced by the action of chlorate of potash on hydrochlorate of aniline. The conditions then become similar to those in Lightfoot's process, with this difference, that the soluble salt of copper does not exist in the mixture before it is impressed on the fabric."

REPORT UPON THE "ANILINE BLACK,"

Presented by MONSIEUR THEODORE SCHNEIDER, on behalf of the Chemical Committee, Mulhouse Industrial Society, Sitting of the 26th April, 1865.

GENTLEMEN,

You have at your meeting of the 30th November last, in consequence of an interesting report by Dr. Penot for the Chemical Committee, divided the premium given by Daniel Dollfus, for a reward to those scientific men whose labours should have most powerfully contributed to the improvement of one of the finest conquests of modern industrial knowledge.

Whilst adopting the conclusions of the reporter, you have awarded a gold medal of honour to Mr. Runge, and four gold medals of a smaller size to Messrs. Bechamp, Perkin, Hoffmann and Verguin. If you have not awarded any recompense to other chemists who have succeeded in obtaining from aniline other colours besides the violet and the red, such as the blue, the green, the black, etc., it is not on account of your having under-valued the great importance of these discoveries, whereby the series of brilliant colours derived from aniline may be said to have been completed. But it is owing to the fact that they seemed, on the one hand, to be a mere immediate consequence of the first discoveries, and that, on the other hand, they were so recent, and had hardly had time to be thoroughly tried and their value ascertained from the practical use of them. However, the "Aniline Black" has since that time been sufficiently proved.

Your Chemical Committee is proud in being able to corroborate this fact, and they have deputed Mr. Schutzenberger and myself to present to you the historical sketch of this new coloured product.

From all the information gathered from the various members of the Chemical Committee, it is ascertained that to Mr. John Lightfoot, of Accrington, belongs the discovery of the "Aniline Black." The process of this chemist was patented

in France, in January, 1863, and sold to the firm of J. J. Müller and Co., Basle, Switzerland, in January, 1863.

The method whereby Mr. Lightfoot obtains Aniline Black on cotton, consists in printing with a mixture of hydrochlorate of aniline, chlorate of potash, chloride of copper, sal-ammoniac, acetic acid, and starch paste; to expose the fabric in the drying-room, and to wash them afterwards in water feebly alkaline. It is worthy of remark that the colour does not exist at the time of printing the stuff, but that it is generated gradually upon the cloth itself, in the ageing-room, under the influence of both oxidizers, the chlorate of potash and the chloride of copper. This new colour, which was soon used in England, Switzerland, Germany and France, was, however, also soon abandoned in Alsace, almost completely on account of the serious drawbacks which were attending its use. The (colour) mixture, in fact, corroded the doctors and the rollers, and weakened considerably the fibre of the cloth, and could not be kept for any length of time at ordinary temperatures. The corrosion of the doctors and rollers may be avoided, it is true, by printing or padding directly upon the cloth the salt of copper, instead of adding it to the mixture. This modification, which was already mentioned in the Lightfoot patent, and the advantages of which were acknowledged by several firms in Alsace, consists in printing (or padding) the cloth with a solution of copper salt, and then printing afterwards the mixture of chlorate of potash and aniline salt. This double printing is not only expensive, but it limits the number of colours which may be associated with the black thus produced, and has, besides, the inconveniences of all processes requiring the previous preparation of cloth. It will not surprise us, therefore, to see the trade receiving favourably, towards the end of 1863, a new method for the production of Aniline Black, which, at the first sight, seemed free from the defects inherent to the Lightfoot's process.

Mr. Cordillot, by substituting, in the mixture of the English chemist, the red prussiate of ammonia (Ferridcyanide of ammonia) for the copper chloride, did avoid the corrosion of the doctors and rollers; but, unfortunately, these real

advantages were obtained at the expense of fresh inconveniences nearly as serious as those which they were to remedy. The mixture of Mr. Cordillot was much dearer, could be preserved only a very short time, and required for its oxidation a higher temperature, not easily obtained in the ageing room of the calico printing establishments. Moreover, it was more difficult by this process to obtain a good black, and often produced "*stains*" (marking off) during the washing or the starching. Such was the state of the question when the process of Mr. Lauth appeared, and which is generally considered as the most practical and best suited for the trade, of all those which have been proposed hitherto, yet offering still numerous inconveniences, such as the difficulty of printing this black with mordants, with steam colours, and with catechu, which are used with good results in certain kinds or styles of work. This method is based upon the ingenious idea of printing, along with the aniline salt and the chlorate of potash, an insoluble compound of copper, which is, therefore, without action upon the doctors and rollers, but becoming finally soluble on the cloth.

This compound is the "copper sulphide," prepared artificially as follows: Flowers of sulphur are dissolved in caustic soda, the liquor obtained is poured into a solution of "copper sulphate" at a temperature of 75° C. The precipitate of "copper sulphide" is collected upon a filter and washed.

The mixture of Lauth, being composed of a salt of aniline, of chlorate of potash, and of sulphide of copper, which, by oxidation is transformed into "sulphate," evidently comes to the same final requirements as the Lightfoot process. Experience has shown that the indirect oxidising properties of sulphide of copper and its applications are not limited, as the author had foreseen it, to the special case of Aniline Black, but that this compound may be advantageously utilised for other kinds of work, such as the oxidising of catechu; for example:—The mixture can be preserved a tolerable length of time; it oxidises easily; it is very stable in the air, and does not corrode doctors or rollers. The process just mentioned is described in general terms in a memoir sent for competition in 1865, bearing for its epigraph the motto,

"Force and Matter." The author of this work, who can evidently be no other than Mr. Lauth, competes for the prize relating to the discovery of any process useful in calico printing; and he seems to think that the detailed description of his process is not necessary, since it is now well known and generally adopted in Alsace. He merely thinks it necessary to insist upon the advantages of his process above mentioned.

Your Committee thus finding themselves in the consideration of a process which was not an original one, but only a happy modification of the Lightfoot process, has thought that a recompense for an improvement should not be awarded without also crowning the author of the first discovery.

Your Committee recommends, therefore, that a medal of honour be awarded to Mr. Lightfoot, for his discovery of the "Aniline Black;" and to award to Mr. Lauth a first class medal, for his improvement of the process of Mr. Lightfoot, and for having endowed the trade with a new *oxidiser*, viz., the "copper sulphide." Your Committee requests besides that the present report be printed.

A. Paraf, 1865, 22nd March, No. 804.

"This invention consists in the production of a black colour upon cotton, in which I use a salt of aniline, or its homologues, or a mixture of the same decomposed by any salt or mineral acid, organic acid, or a mixture thereof, which are not liable to injure the fabrics or yarns, in conjunction with a mixture of the chlorates of the alkalies."

The acid used is Fluo-silicic, and the following reaction takes place:—

"The fluo-silicic acid forms fluo-silicate of potash with the potash of the chlorate, the chloric acid coming free; one part of that chloric acid goes to the aniline of the chloride of aniline, the other part transforms the chloride of the same salt of aniline in free chlorine, and this mixture of chloric acid and free chlorine upon aniline gives the black."

Report says that this colour was perfectly impracticable,

until the "black liquor," mentioned in the patent, received about 3 per cent. of a copper salt.

John Lightfoot, 1865, 11th September, No. 2,327.

"For the purpose of oxidizing the deoxidizing properties of the animal fibres and substances thereby rendering them capable of receiving the aniline black."

This process has not been much used, on account of its requiring a different apparatus and *modus operandi*, and also on account of its slight extra cost. When "aniline" becomes a little cheaper, the above process will probably be adopted, since it avoids twice dyeing, as now generally practised; for by preparing the mixture of cotton, wool, silk, or other animal substance, as above stated, they will both take the black dye at one and the same time.

Extract from the MONITEUR DE LA TEINTURE, "DYEING WOOL WITH ANILINE BLACK," by MR. LIGHTFOOT, from the MONITEUR DE LA TEINTURE ET DE LA FABRICATION DES TISSUS, for March 20th, 1867.

"Aniline Black, which has been so extensively applied, had not hitherto been fixed on wool. By whatever process wool may be dyed, the black never develops itself to the requisite intensity, and in many instances only a kind of brown is obtained, instead of the fine blacks which can be noticed on cotton cloths. This negative result (failure) is ascribed to the reducing action of wool. The process of Mr. Lightfoot confirms these views, since it consists in a preparatory oxidation of the fibres or tissues to be dyed or printed. In the first place, a solution is prepared with one kilogramme of dry lime-hypochlorite to ten litres of water, for every kilogramme of wool. This bath is composed thus:—

Water	60 litres.
Solution chloride of lime	1 kilogramme and 300 grammes.
Hydrochloric acid	180 grammes.

"The temperature of the bath is raised to 38° Centigrade, and the wool is worked in it for twenty or thirty minutes, until it has acquired a yellowish colour; it is then withdrawn, completely washed and dried. Fibres or tissues thus prepared are then treated

in the ordinary manner ; they are dyed or printed with the Light-foot patent black, or with that of Lauth ; then ageing and washing, either with weak soap lather or with chromate."

The following experiment proves that wool prepared as above described is really oxidised:—Pour into two test tubes a weak solution of potash permanganate, add to one a sample of wool unprepared ; the solution in this first tube will be decolorized and reduced instantaneously, whilst the other with its sample of prepared wool as above described will retain its purple colour.

"Mr. Lightfoot applies his process not only to woollen fabrics but also to mixtures of wool and cotton. When a uniform black is wanted, the plan of Monsieur Camille Koechlin may be followed, after oxidizing the wool as stated before. It is to be (soaked) steeped in the following mixture:—

Water	25 litres.
Potassa chlorate	1 kilogramme.
Ammonia chloride	1 "
Copper chloride	1 "
Aniline (oily alkaloid) . .	2 "
Hydro-chloric acid	2 "

"After this dye, the threads or the cloth are to hang in a stove with moisture, and heated from 20° to 25° Centigrade, where oxydation takes place. The black will be generated in about twenty-four hours. The operation is concluded by washing with weak soap lather, or by passing through a dilute solution of bichromate of potash."

James Higgin, 1866, 27th March, No. 897.

"Producing black and other shades from aniline by the use of chromates or chromites of metals along with other agents. The chromate of copper I have found to be a useful agent in producing shades from grey to black."

A. Paraf, 1866, 26th April, No. 1,174.

"I mix a salt of aniline, and the brown binocide of chromium,

either alone or in conjunction with a chlorate, and such mixtures printed upon cloth, produce fast aniline black by ageing."

James Higgin, 1868, 27th July, No. 2,351.

"Making a solution of aniline by mixing it with a solution of a metallic salt, such as the chlorides of iron, of tin, or of chromium, and the use 'of the salt of copper, termed disulphocyanide.'"

Large quantities of the disulphocyanide of copper have been used in the production of Aniline Black.

When newly made and mixed, it is entirely without action upon the steel doctor, and even resists its own decomposition by the aniline salt for a considerable time.

It is a much less powerful agent in producing the Aniline Black than the sulphide of copper.

The following translation of the article on Aniline Black, in "Wurtz's Chemical Dictionary," will form a *résumé* of the several processes up to the end of 1866:—

"ANILINE BLACK.—'Moniteur Scientifique,' 1863, page 530 (E. Kopp); *ibid.*, 1864, pages 433, 568, 654; *ibid.*, 1865, pages 68, 467, 969, 769; *ibid.*, 1866, pages 257, 258, 259. 'Bull. de la Société Chimique,' 1865 t. II., page 488; *ibid.*, 1866, t. I., page 90; *ibid.*, 1866, page 235. 'Bull. de la Société Industrielle,' April, 1865, 176. 'Report of Schneider,' 'Bull. de la Société d'encouragement, 1866, page 75. 'Balard's Report.'

"Aniline Black forms, in the class of aniline colours, a separate group. Its method of generation, its resistance to physical and chemical agents gives it a special character. Thus, instead of being prepared in the laboratories for chemical products, like mauveine, rosaline, Lyons blue, etc., it is produced directly on the tissue, by printing a colourless mixture, the elements of which re-act gradually upon one another in determining the formation of the black.

"Another special character of the Aniline Black is the little affinity it manifests for animal fibres, whilst, on the contrary, it fixes itself on cotton with the greatest facility.

"HISTORY.—For the origin of Aniline Black, we may commence

with the experiments of Fritzsche, who reports that, in adding a solution of chlorate of potash to hydrochlorate of aniline, an abundant precipitate of a very dark blue indigo was formed after a certain time. This body would have for composition $C^{24}H^{10}Ag^2ClO(?)$.—*Journ. für prakt. Chem.*, t. xxviii., p. 202.

"This same substance is obtained, according to Hofmann, by adding a solution of chloric acid to a hydrochlorate of aniline."—*Moniteur Scientifique*, 1861, p. 75 : *Ann. der Chem. u Pharm.*, t. xliii., p. 66.

"Willm had the first idea of applying this re-action to the colouring of vegetable fibres. In impregnating a cotton tissue with a mixture of chlorate of potash and hydrochlorate of aniline (a colourless mixture), he saw, after some time, this mixture change into a dark green colour, fixed fast on the fibre."—*Memoir deposited at the Industrial Society of Mulhouse, February, 1860*, and *Bull. of Société Chimique*, 1860, p. 206.

"This green, as far as we can see, depends upon the degree of acidity entirely for its shade in the neutral state, which is always the final stage of colours upon tissues. This composition is of a bluish grey.

Subsequently Calvert, Lowe, and Clift applied these re-actions to the manufacture of printed cloths, and published the following receipt:—Print a mixture of 60 kilogrammes weight of starch, 3 kilogs of tartrate or of hydrochlorate of aniline, 1 kilog of chlorate of potash. Age it from 24 to 48 hours. Then the colour, which was colourless at the time of impression, having become green, pass the tissue through a solution of alkali; the green shade then becomes blue.—*Patent of 11th June, 1860*.

"These shades of blue and green, designated emeraldine and azuline, do not excite any great industrial interest, on account of their little brilliancy.

"E. Kopp has studied these different products; he maintains that they only constitute one single substance, the shade of which depends upon the neutrality or the acidity of the mixture; that the colours obtained upon the tissue are very fast, and resist all action of the sun, soap, and all the operations of madder dyeing; reducing agents are equally without effect upon them."—*Scientific Review*, 1861, p. 75.

"To prepare this body in the state of a precipitate, Kopp mixes in a crucible 10 p. of aniline, 50 p. hydro-chloric acid, 50 p. of water, 2 p. of chlorate of potash. The reaction is accomplished

slowly, by an ordinary temperature, and lasts several days. If it is heated, it becomes violent, and is changed more quickly.

"Kopp has observed the formation of emeraldine in several other ways, amongst others by the action of ferricyanide of potash, or perchloride of iron on a salt of aniline. This last reaction has also been noticed by Jules Persoz (*Pelnise and Frémy*, 1865, t. III., p. 291).

"Scheurer Kestner obtains the emeraldine by the action of hydro-chloric acid and the peroxide of Manganese, or by the hydro-chloric acid and nitrate of iron (*Bull. of the Industrial Society of Mulhouse*, 27 June, 1860). Ch. Lauth prepares it by treating 1 p. of aniline by 10 p. of hydrochloric acid, diluted with 100 p. of water, and adding gradually 2 p. of peroxide of barium (*Moniteur Scientifique*, 1861, p. 79).

"Such was the state of the question when John Lightfoot, of Accrington, created the Aniline Black, 28th January, 1863. Patent, (France), No. 57,192.

Lightfoot printed on the cloth a mixture of 1 litre of starch paste, 25 grammes of chlorate of potash, 50 grammes of aniline, 50 grammes of hydrochloric acid, 50 grammes of perchloride of copper s.g. 1.44, 25 grammes of sal ammoniac, 12 grammes of acetic acid.

"The printed cloths are carefully dried, then carried to the ageing rooms, or simply exposed to the air for two or three days. The impressions, colourless at first, are then of a deep green. It is only necessary to wash the cloth in water, or in weak alkali, to change the green into a beautiful blue black.

"The brilliancy of the black, its permanency, and its cheapness, readily explains the importance of the discovery of Lightfoot, and the ardour with which every one began to apply it. Unfortunately, the process of Lightfoot presented some serious difficulties, which caused it to be abandoned. The acid colour attacked and changed the fibre of the cloth. It also decomposed rapidly before use, and the presence of the soluble copper salt caused the metal to deposit itself on the steel doctor, and hence caused *doctor streaks*, injuries which are of more consequence as they could not be seen till the colour was developed, which then resists all bleaching agents.

"Camille Kœchlin, the able chemist of Mulhouse, obviated most of these inconveniences, by padding the tissue in a salt of copper, and printing on this prepared cloth a mixture of chlorate of potash and hydrochlorate of aniline.

"Besides the expense of this process and special apparatus re-

quired, it limited very much the styles and the number of colours that could be used with the black.

"Cordillot, about the end of 1863, made known a new process for producing the Aniline Black. He replaced the chloride of copper in Lightfoot's colour by the ferridcyanide of ammonium, and avoided in this way many of the defects inherent to the first process; but the advantages of this process of Cordillot were only obtained at the cost of other serious inconveniences. The colour is dear, decomposes rapidly, and requires for its development on the cloth a higher temperature than that of the ordinary ageing rooms. This process of Cordillot was also abandoned, and at this moment it was thought that the splendid discovery of Lightfoot would remain unfruitful.

"Charles Lauth is the author of the actual process generally followed in the use of Aniline Black, and which he gave to the manufacturers of Mulhouse early in 1864.

"Lauth recognised the fact, after many trials, that the presence of copper, or of a metal easily reducible, is indispensable to the production of the black; and on the other part, as practice had proved that the metallic salts, and especially those of copper, were not possible to use, he had recourse to the use of an insoluble compound of copper, inactive, consequently, at the moment of its impression, but ultimately soluble and active.

"The sulphide of copper fulfils this end, and is now employed not only for the Aniline Black, but in a great many oxidations on tissues.

"The receipt of Lauth is as follows:—10 litres of starch paste, 350 grammes of chlorate of potash, 300 grammes of sulphide of copper in paste, 300 grammes of sal ammoniac, and 800 grammes of hydrochlorate of aniline. The printed stuff is aged, then washed in water or alkali.

"The process of Lauth permitted industry to use Lightfoot's beautiful discovery, and from thence it has been applied on a large scale.

"Camille Kœchlin came at last to put the final touch of construction to this edifice, raised with so much trouble, by replacing the hydrochlorate of aniline by the tartrate, a salt absolutely harmless upon the most delicate tissue, and which has also this great advantage over the hydrochlorate of aniline, that it does not attack the mordants by the side of which it is printed. The tartrate of aniline would be alone incapable of producing the black, but in presence of

the sal ammoniac, of which the proportion is considerably augmented, there is gradually a double decomposition on the cloth, and formation of hydrochlorate. At this moment the conditions are the same as the Lauth process.

“Camille Kochlin prepares this colour as follows :—

“Boil together—

Water		10 litres.
Starch		2 kilogrammes.
Torrefied starch		2 ”
Aniline		2 ”
Sal ammoniac		1 ”
Chlorate of potash		1 ”

When to be used, add cold—

Sulphide of copper paste		1 ”
Tartaric acid		2 ”

“The sulphide of copper can be prepared by dissolving, cold, 1 kilogramme of flowers of sulphur in 4 litres of caustic soda, at 38° AB, and adding this to a solution of sulphate of copper, 5 kilogrammes in 120 litres of water at 80°.

“Divers processes have been published since, for the production of Aniline Black. Up to this time, nothing has replaced the sulphide of copper, ‘without which Aniline Black would not be possible at this time.’ (*Camille Kochlin.*)

“Paraf proposed the use of a black without copper, formed exclusively from fluo-silicate of aniline and chlorate of potash. Rosenstiehl advised a mixture of hydrochlorate of aniline and chlorate of ammonia.

“But it has been proved since by Rosenstiehl and Lauth also, that these mixtures will not develop the black unless they are printed with a copper roller. In these cases, a certain quantity of copper is dissolved, and it is to this copper that the formation of the black is due. (*Bull. de la Soc. Indus. de Mulhouse*, Aug. and Nov., 1865, and *Bull. de la Soc. Chim.*, 1866, t. V., p. 90 and 235.) It has been acknowledged that the chlorate of ammonia presents some advantage over the chlorate of potash, and certain manufacturers actually use it with the sulphide of copper.

“Higgins, of Manchester, recommended the use of arseniate, of tungstate or oxide of chrome in the presence of chlorate of potash and hydrochlorate of aniline.—*Patent* 73,054, and *Bull. de la Soc. Chim.*, 1867, t. VII., p. 93.

"We remark, lastly, the Black of Lucas, the composition of which is secret; it is sold as a paste containing all the materials necessary to produce the black, only requiring thickening and printing, when the colour is developed.

"Such are the different processes actually known for the production of Aniline Black.

"This colour at present is extensively used, and is of great importance. The known ability of the Mulhouse printers has overcome the practical difficulties which it offers in certain styles; and the Exhibition, 1867, exhibited Aniline Black in combination with nearly every colour, upon all kinds of tissues, and under conditions the most varied.

"Before long, doubtless this valuable colour will be used for dyeing wool and silk.

"Already Lightfoot has shown that the resistance of affinity the black shows to wool disappears when the wool has been previously oxidised by the chloride of lime. (*Chemical News*, Aug. 1866, p. 59, and *Bull. de la Soc. Chim.*, t. VI., p. 505, 1866.) More recently Jules Persoz has succeeded in dyeing wool by mordanting it in a mixture of bi-chromate of potash and sulphate of copper, then passing it into an acid solution of aniline. All this makes us hope that very soon the black will find its application to animal fibres.

"We know nothing about the composition of Aniline Black.

"Its mode of formation indicates that it is derived from aniline by oxidation.

"This oxidation is produced by the chlorate of potash and the copper compounds, which, successively reduced by the aniline and re-oxidised in contact with the air and the chlorate, serve, doubtless, as the agent between the oxygen and the aniline.

"The sal ammoniac, of which the presence is valuable, if not indispensable acts apparently as the solvent of the copper compounds gradually, as they are formed. It also allows of their prompt reoxidation. Such is, in our opinion, the most simple explanation of the formation of the black, a formation analogous to that of several other colours—catechu, for example. Camille Kœchlin indicated this the first.

"Rosensthiel does not admit that the copper acts as an oxidiser. He thinks that the copper serves to form chlorate of copper, which, of all the chlorates, is most easily decomposed, and that it is only to assist in the decomposition of the chlorate that the presence of

copper is necessary. (*Bull. de la Soc. Indus. Mulhouse*, 29 Nov. 1865.)

“ PROPERTIES OF THE ANILINE BLACK.—The Aniline Black fixed on the cloth is of a beautiful velvet tint. It becomes dark green in contact with strong acids, as well as by long exposure to light. It recovers its original colour by simple washing in water. It is insoluble in all the usual chemical agents. The strongest sulphuric acid will not touch it. Nitric acid changes it into picric acid. Fixed on the tissue, it is exceedingly permanent, resists boiling, soap, and all the operations of madder dyeing.

“ Other properties have been pointed out by Dullo (*Illustr. Gewerbezeit*, 1866, p. 161). This chemist prepared it in paste, mixing 100 grammes of light aniline (the heavy aniline gives brown, not black), with 80 grammes of hydrochloric acid, 10 grammes of peroxide of manganese, and 1000 grammes of water. The precipitate is gathered, washed by decantation, then mixed with ammonia. Its colour then changes from green to black, and by assisting it to absorb the oxygen of the air by proper agitation, the colour is developed through the entire mass.

Dullo tried upon this product the several agents used to reduce indigo, hoping thus to get a soluble black, but without effect. Most of the reducing agents are without action, and those which act (a mixture of glucose and soda for example), give rise to a product as insoluble as the black itself. After the same author, the little affinity of the black for animal fibres should be attributed to the fact that it always precipitates in flakes too voluminous to penetrate into the pores of the fibres.

“ Camille Kœchlin, in his remarkable article on ‘the Black of the Alkalies’ (*Moniteur Scientifique*, t. VII., p. 769), describes a curious property of the Aniline Black.

“ When in contact with a solution of hypochlorite of lime at 8°, the black fades, takes a red shade, then becomes garnet colour. If the action of the chlorine is then stopped, the colour in time returns, and the black, with all its intensity, is re-formed.

“ We refer the reader to this article of C. Kœchlin, who wishes to know in all its details the properties of Aniline Black, as well as the technical difficulties of its application.

The Aniline Black is now sold by Perry and Co., 3, Cheap-side, London, for marking linen, under a license from the proprietor of the Patent.

For all the practical purposes of the calico printer, it is evident that copper, in some shape or other, is the starting point for the formation of the Aniline Black. The acid mixtures of Calvert, Clift and Lowe, or of Paraf, are but grey or deep and intense blues, and varying directly in proportion to their acidity. With acidity comes the corroding of the steel doctor, the dissolution of the copper roller, and destruction of the cloth. The object of the calico printer should be, to use the least possible quantity of acid, an alkaline mixture, if possible, and to use that agent which will produce the black with the least quantity of acid.

In the following experiments, to determine the influence of the several metals upon the aniline salt, I have used what I term a basic salt of aniline, a term which, though not perhaps scientifically correct, will the better explain the condition of the mixed acid and aniline; probably the best explanation is, that the definite chloride of aniline dissolves the aniline added to it.

Table of the different "Salts of Aniline," and their reactions (on sulphate of copper mixed with gum water).

Different salts of aniline.	Aniline, oil of Naptha.	Hydrochloric acid. Sp. gr. 1.15.	Reactions.
Basic chloride aniline	2 parts.	1 part.	Becomes <i>brown</i> and precipitates.
Slightly basic chloride aniline	2 "	1½ "	Becomes an <i>olive green</i> , and does not precipitate.
Neutral chloride aniline	2 "	1¾ "	Becomes a <i>yellowish green</i> , does not precipitate.
Acid chloride aniline	2 "	2 "	This remains clear, the colour not changed.

The best test to determine excess of acidity in the chloride of aniline is the magenta paper, called Dale's test, bibulous paper, soaked in a solution of magenta to give a pink colour. The slightest excess of acid converts the pink into yellow.

The experimental normal colour A. was made as follows :—

Water	1 gall.	} Boil and cool.
Calcined starch	4 lbs.	
Chlorate of ammonia	12 ozs.	
Basic chloride of aniline (8 of aniline, 6 of acid).		} 1½ pints.

This colour was printed with a wood block upon a piece of new white bleached calico, and whilst the calico was still wet with the colour the following metals and metallic earths were placed upon it, and left there for 15 minutes:—Copper, iron, vanadium, uranium, nickel, lead, zinc, antimony, tin, manganese, chromium, bismuth, arsenic, titanium, tungsten, cadmium, tellurium, molybdenum, mercury, silver, gold, platinum, palladium, rhodium, iridium, aluminium, osmium, cobalt, ruthenium, thallium, magnesium, indium, rubidium, cerium, glucium, zirconium, lanthanum, didymium, erbium, yttrium, selenium, tantalum, niobium.

The cloth was aged for 12 hours in a warm moist room, then washed in soap and water.

The result was this, the greatest development of the black was due to the vanadium, next in order was copper, then uranium, and, lastly, iron. Except very slight shades of blue, no action was apparent from any of the other metals.

In illustration of the effect of copper, the following experiment was made:—Colour A. was printed upon a piece of calico with a wood block, and whilst still wet a shilling and sovereign, previously cleaned in nitric acid and water, were placed upon the cloth for 15 minutes; the calico was aged 12 hours and washed, no trace was shown of the contact of the coin. The same coins were then placed in a bag with copper coins, and slightly shaken up with them. Applied then in the same way to the calico, and under the same conditions, the sovereign gave a dark slate, and the shilling an all but black colour. The mere rolling of a copper coin over the wetted calico is sufficient to induce the formation of the black.

An experiment of Mr. Morgan-Brown's would seem to prove that this action is due to an actual solution of the copper, for

if the piece of copper be protected with a piece of zinc, so as to form a one-cell battery, the contact of the copper with the calico, even in half an hour's duration, produces no effect whatever.

I have myself tried other metals in contact with the copper, such as tin, lead, bismuth, and the action of the copper has been arrested entirely.

Whether the action from the copper is due to electrical action, catalysis, or actual change of its combination repeated over and over again, the fact is not to be disputed, that the most infinitesimal quantity of the four metals—copper, iron, vanadium, uranium—is sufficient in the chloride of aniline and chlorate of potash solutions to set up a state of things that will gradually produce the black.

It is very doubtful if any trace of the copper will remain in the calico, after the formation of the black. If care is taken to thoroughly wash out the thickening matter in the calico by dilute sulphuric acid, or an infusion of hot water and malt, the incineration of the cloth, and subsequent treatment for copper, scarcely gives a trace of its presence.

The salts of the metals, copper, iron, vanadium, uranium, act in the same way as their respective metals; whilst the salts of the metals named as having no action, behave inertly, that is, if care is taken to insure the absence of the four active metals. To avoid the presence of copper or iron in these experiments is a most difficult matter.

It is scarcely possible to find three inches square of calico that will not, under the influence of the normal solution A. and 24 hours' ageing, give the most evident signs of the iron or copper in the tissue, resulting, perhaps, from the machinery through which it has passed in the course of manufacture.

The whitest paper contains iron by many degrees in excess of the quantity that could be abstracted from the iron placed in contact with the calico, as described in the preceding experiments. In the whole range of chemistry there is scarcely a parallel case of such marked results obtained from such infinitesimal quantities. Small as the quantity of copper is that will produce the Aniline Black, it is very different in the practice of the calico printer. Other elements there, as time,

intensity, and stability, require much larger quantities. The attempts made to dispense with the copper have hitherto always reverted to its re-employment, and demonstrated that the copper roller will not alone furnish the quantity of copper needed for a practical result.

The successful working of Aniline Black depends upon fulfilling the following conditions :—

1st. Absence of injurious acidity, and consequent destruction of the cloth.

2nd. Ageing at the lowest temperature, to reduce the effect of the acid on the cloth.

3rd. That the steel doctor shall not be affected by the mixture.

4th. That the black shall not be liable to change.

5th. That it shall be adapted to every known style of printing.

6th. Protection to the black cloths.

My experiments and practice of the last two years enable me to say that all these conditions are reasonably fulfilled in the practical working at Lower House Print Works.

Many of those improvements are embodied in a Patent taken out by me on the 12th April, 1870, and are based upon the use of a basic salt of aniline, the use of chlorate of ammonia, and especial care taken in the preparation and management of the sulphide of copper. In the new black resulting therefrom the tendency to change in an acid atmosphere has been almost entirely prevented.

The cloth is not in the least degree weakened.

The steel doctors are not affected, and the process is adapted to nearly every style of printing.



